Could an efficient WGS catalyst be useful in the CO-PrOx reaction?

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ABSTRACT

This work presents an evaluation of a high performance series of water gas shift (WGS) catalysts in the preferential CO oxidation reaction (PrOx) in order to examine the applicability of the same catalyst for both processes as a first step for coupling both reactions in a single process. Gold based catalysts are applied in an extensive study of the CO-PrOx reaction parameters, such as λ, WHSV, CO concentration and $[H_2O]/[CO_2]$ ratio in order to obtain the best activity/selectivity balance. CO and H_2 oxidation reactions were treated separately in order to establish the degree of CO/H_2 oxidation competition. Additionally the catalysts behavior in the CO-PrOx parallel reactions such a WGS and RWGS have been also carried out to analyze their effect on product composition.

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1. Introduction

The hydrogen-fueled polymer electrolyte membrane fuel cell (PEMFC) is considered a very promising candidate to directly convert chemical into electrical energy [1]. PEMFCs appear to be a viable technology for small-scale electricity production as required for electric vehicles and residential power generators due to their advantageous features, such as low-operating temperature (80–200 °C), sustained operation at high current density, low weight, and compactness, potential for low cost, fast start-up and suitability for intermittent operation [2]. These small-scale units depend on processing a hydrocarbon fuel for producing a H_2-rich product that fuels PEMFCs. Fuel processors convert liquid hydrocarbons, the volumetric energy content of which is much larger than that of bottled hydrogen, into an almost CO-free H_2-rich product through the coupling of several catalytic reactions, such as reforming, usually steam reforming, WGS, PrOx and/or methanation ones [3–6]. The water gas shift reaction ($CO + H_2O \leftrightarrow CO_2 + H_2$) is a critical step in fuel processors for preliminary CO clean-up and additional hydrogen generation prior to the CO preferential oxidation or methanation step [4–7]. WGS units are placed downstream of the reformer to lower the CO content and improve the H_2 yield. However, WGS is an equilibrium-limited reaction and CO

concentrations below 10 ppm (requisite for the PEMFC anode) cannot be reached even with high H_2O/CO ratios at reaction temperatures above 200 °C [8]. Therefore, an additional CO removal process is always required.

Preferential CO oxidation of the pre-cleaned reformate stream (PrOx) with air is one of the most effective methods for CO abatement from the reformate stream prior to its introduction in the PEM cell [9]. High CO oxidation activities coupled with low hydrogen ones (at the desired oxidation temperature) are essential requirements for the PrOx catalysts [10,11].

In recent years, there has been great interest in the CO oxidation reaction over gold-based catalysts [12–14]. Despite bulk metallic gold being a very poor catalyst in this reaction, supported gold nanoparticles are able to eliminate CO even at sub-ambient temperatures [15,16]. Nanogold catalysts are promising candidates for the PrOx reaction for two main reasons: (i) they show extraordinarily high activity in the low temperature range, which is appropriate for fuel cell applications, (ii) the rate of CO oxidation exceeds that of hydrogen oxidation in the relevant temperature range [17,18]. In addition to high activity and selectivity, a suitable PrOx catalyst must also tolerate high amounts of CO_2 and H_2O present in the reformate stream [19]. Generally, the presence of both CO_2 and H_2O diminishes CO conversion, especially at low temperatures [20,21]. An excellent WGS catalyst withstands high amount of H_2O. The ability of a catalyst to admit large ranges of CO_2 concentrations in both WGS and PrOx, generally depends on its composition, specifically on the support nature, with acid supports more

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resistant to deactivation. It was recently reported by Tabakova et al. [2] that an Au/CeO_2–Fe_2O_3 system can successfully tolerate CO_2 and H_2O allowing good performance in the PrOx reaction. For the WGS reaction an efficient catalyst based on a similar system, Au/CeO_2–FeO_x/Al_2O_3 was also reported [22].

Following the concept of process intensification, it would be interesting to design a reactor where both reactions (PrOx and WGS) are successfully carried out in a single catalytic wall reactor by careful control of the temperature profile of the reactor and the reactant insertion zones, this way doing away with one reactor on the overall CO clean-up process (Scheme 1). The development of such an advanced reactor may reduce cost and system volume allowing the adaptation of this type of fuel processor to smaller devices for portable applications. Considering the experimental conditions in which WGS and PrOx take place, i.e. space velocity, temperature window, equilibrium limitations etc., coupling these reactions in a single reactor is a great challenge. Nevertheless, as a first step toward process intensification, the preparation of one efficient catalyst for both processes is required.

Considering the promising features of gold based systems for these reactions, the aim of this work is to study the possibilities of use of a gold-based WGS catalyst in the PrOx reaction with the idea of facilitating the possible future coupling of these reactions in a single reactor.

2. Experimental

2.1. Catalyst preparation

The supports were prepared by impregnation of $Ce(NO_3)_3 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ (Aldrich) on γ-alumina powder (Sasol) in order to obtain a cerium-iron mixed oxide dispersed on alumina. The precursor amounts were calculated in such a way so that the final loading of CeO_2, FeO_x or CeO_2–FeO_x solid solution were 15 wt.% of the final solid. In order to ensure the production of a FeO_x–CeO_2 solid solution, the FeO_x content was always maintained below 3 wt.% [22]. Gold (2 wt.% nominal) was deposited by the direct anionic exchange method, assisted by NH_3, as described elsewhere [23].

In the adopted nomenclature, oxygen is omitted for simplification and the FeO_x contents are expressed as the theoretical catalyst loading. For example, the Au/CeFe0.5/Al solid contains 2 wt.% Au loading over a CeFe mixed oxide in which the FeO_x content is 0.5 wt.% and CeO_2 loading is approximately 14.5 wt.%, deposited on Al_2O_3 support.

2.2. Catalytic activity and selectivity

2.2.1. Preferential CO oxidation

PrOx reaction was carried out at atmospheric pressure on a cylindrical fixed bed quartz reactor (9 mm inner diameter) at $60,000 \, cm^3 \, g_{cat}^{-1} \, h^{-1}$. For each test, 100 mg of catalyst sieved between 100–200 μm were loaded in the reactor. To minimize, as far as possible, the thermal effects due to the oxidation reaction, the samples were diluted in quartz. The feed flow rate was $100 \, cm^3 \, min^{-1}$ containing 1% CO, 1.5% O_2, 50% H_2 and He as a balance. To study the effect of H_2O and CO_2 on catalyst activity and selectivity, 10% of each compound was added in the feed. Prior to catalytic measurements, the samples were treated under a $100 \, cm^3 \, min^{-1}$ flow of 21% O_2 in He, at 300 °C for 1 h. The influence of the λ parameter ($\lambda = 2[O_2]/[CO]$) was studied varying λ from 1 to 4 conserving 1% of CO in all the cases. The influence of space velocity was studied by varying the WHSV between 12,000 and $120,000 \, cm^3 \, g_{cat}^{-1} \, h^{-1}$. Water was added to the dry gas stream via a HPLC pump (Gilson 307). Product and reactant analyses were

carried out by a gas chromatograph (ShimadzuGC-14B) equipped with a TCD detector.

The CO conversion was calculated according to Eq. (1) where CO_{in} is the CO concentration in the inlet and CO_{out} is the one at the outlet:

$$CO \, conversion \, (\%) = \frac{CO_{in} - CO_{out}}{CO_{in}} \times 100 \qquad (1)$$

The O_2 selectivity towards CO_2 formation was calculated with Eq. (2). O_{2in} corresponds to oxygen in the inlet and O_{2out} to the one at the outlet.

$$O_2 selectivity \, (\%) = \frac{(CO_{in} - CO_{out}) \times 100}{2 \times (O_{2in} - O_{2out})} \qquad (2)$$

2.2.2. CO and H_2 oxidation

CO and hydrogen oxidation were carried out at atmospheric pressure in a stainless steel fixed bed reactor (9 mm inner diameter) at 30,000, 60,000 and $120,000 \, cm^3 \, g_{cat}^{-1} \, h^{-1}$. The composition of the CO oxidation stream was 1% CO, 1.5% O_2 and N_2 as balance, while for H_2 oxidation the reactant stream was 1.5% O_2, 50% H_2 balanced in N_2. The catalyst (100 mg, $100 < \phi < 200 \, \mu$m) was diluted with crushed glass particles in the same particle size range forming a bed of about 5 mm in length. Products and reactants were analyzed by on-line gas chromatography (Agilent® 6890) equipped with a HP PLOT Q and HP-5 columns and a TCD detector. Prior to catalytic measurements, the samples were treated under a $100 \, cm^3 \, min^{-1}$ flow of 21% O_2 in N_2, at 300 °C for 1 h.

2.2.3. Water gas shift and reverse water gas shift reactions

The study of the water gas shift reaction was carried out at atmospheric pressure in a stainless steel fixed bed reactor (7.5 mm inner diameter) at $60,000 \, cm^3 \, g_{cat}^{-1} \, h^{-1}$. A $100 \, cm^3 \, min^{-1}$ reaction mixture composed of 1% CO, 10% H_2O and N_2 as balance was flowed over 100 mg of catalyst. For the reverse water gas shift, the reaction flow was composed of 10% CO_2, 50% H_2 and N_2 as balance and the same space velocity was used. Products and reactants were analyzed by on-line URAS 2G CO, CO_2 gas analyzers (ABB A02020)

2.2.4. CO/H_2 and CO/O_2/CO_2/CO pulses

For pulse experiments 100 mg of catalyst was loaded into a U-shaped quartz reactor. The samples were first activated in an O_2/He flow ($50 \, cm^3 \, min^{-1}$) at 300 °C during 1 h. After cooling and stabilizing the temperature, 10 O_2 pulses followed by 10 H_2 pulses (1 cm^3 each) were sent in order to reproduce as far as possible the PrOx reaction conditions. After that, CO–H_2 pulses were alternatively introduced in the reactor every 2 min. The gas composition at the exit of the reactor was analyzed by a mass spectrometer PFEIFFER Vacuum Prisma Plus controlled by the program Quadera®.

To study the inhibitory effect of CO_2, a series of CO/O_2/CO_2/CO pulses were also studied. The sample was pretreated at 300 °C as explained above. Afterwards, the sample was cooled and the temperature was fixed at 150 °C. CO/O_2/CO_2/CO pulses (1 cm^3 each) were sent and the gas composition at the exit of the reactor was analyzed with the same mass spectrometer.

3. Results and discussion

3.1. Effect of iron in the PrOx reaction

Full details of characterization and preparation of the studied catalysts have been given elsewhere [22]. Although, they are not subject of this study they will be further used for correlating the results obtained in the present work with the catalyst properties. Nevertheless, it is worth to briefly summarize the main
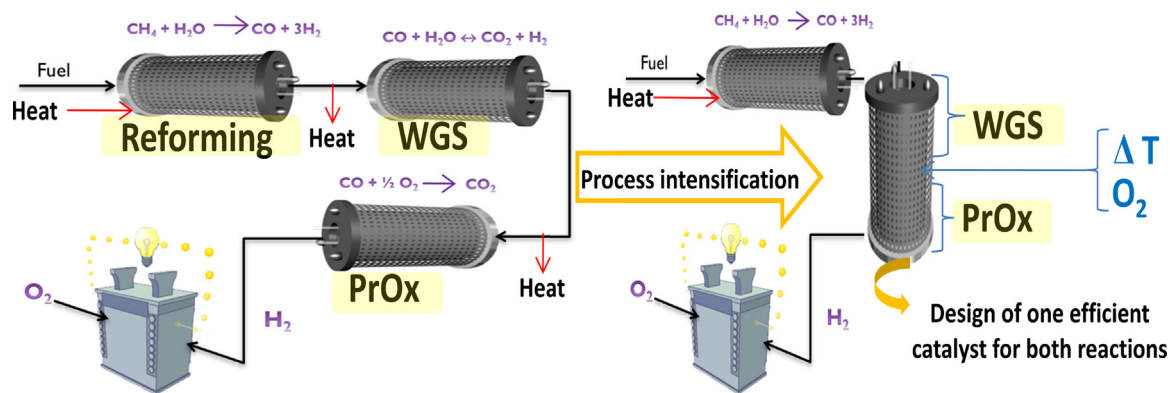
Scheme 1. H_2 clean-up process via WGS–PrOx reactions.

results obtained in such previous work. In that study a high variation of WGS activity of Au/CeFeX/Al samples (with X varying from 0–3 wt.%) with similar gold particle size was reported, depending on the extent of Ce–Fe interaction. The WGS activity is governed not only by the presence of gold and its particle size but also by the formation of a ceria–iron solid solution. The activity enhancement is related to a Ce–Fe synergetic effect that favors water activation, either by the redox or associative mechanism. Deactivation of gold catalysts was observed and was attributed principally to the formation of carbonate and formate species, identified by Diffuse Reflectance Infrared Spectroscopy (DRIFT), which limit the accessibility of the support active sites for the activation of water.

The use of the same series of catalysts in the preferential CO oxidation leads to the activity and selectivity results presented in Fig. 1A and B, respectively. All catalysts are very active at low temperature. In general, a decrease in CO conversion is observed with increase of temperature, due to the increase of the hydrogen oxidation rate. As in WGS, the PrOx activity seems to be influenced by the catalyst composition, more precisely by the nature of the support. The Au/Al$_2$O$_3$ catalyst was the least active followed by Au/Fe/Al. On the other hand, Au/Ce/Al showed high activity for the preferential CO oxidation. This result points to the need of an active support to obtain a good CO abatement performance. The role of an active support like ceria is double, firstly it supplies oxygen to the CO oxidation process and secondly, the structural defects of ceria namely oxygen vacancies, may act as oxygen activation sites leading to more reactive oxygen species that further react with CO. The Au/Ce/Al catalytic properties are enhanced when iron is added to the catalyst. The promotion of iron to ceria is evidenced in terms of the activity improvement, especially at low

temperatures. Au/CeFe2/Al is the most active system in the temperature range 90–120 °C where an efficient PrOx catalyst should operate for fuel cell applications. This sample achieved 92% CO conversion and 40% O_2 selectivity at low temperature (50 °C) and 80% CO conversion with 33% of oxygen selectivity towards CO_2 at 110 °C. The same sample, Au/CeFe2/Al, was also the most efficient catalyst within the examined series in the WGS reaction, showing high yield of hydrogen in the medium temperature WGS window (160–350 °C), attributed to the strongest Ce–Fe interaction resulting in an enhancement of the number of oxygen vacancies and therefore promoted redox properties. Indeed, in a recent paper, it has been demonstrated that the oxygen storage complete capacity (OSCC) and the oxygen storage capacity (OSC) of gold catalysts supported on ceria are considerably promoted by the addition of iron [24]. The numbers of atomic oxygen layers that participate in the redox process is higher when iron is employed as a ceria dopant. The inclusion of iron in the ceria lattice alters the covalent character of Ce—O bonds favoring oxygen mobility and leading to promising materials for CO oxidation.

Regarding selectivity, the trend is similar for all catalysts: the higher the temperature, the lower the selectivity towards CO oxidation pointing out that H_2 oxidation starts already from low temperatures and becomes more important when the temperature is increased. Au/Al sample was the least selective within the series. This can be correlated again with the redox properties of the supports in the PrOx reaction. As can be seen in Fig. 1B, all the ceria containing samples presented similar selectivity profiles while Au/Al and Au/Fe/Al are slightly different. It seems that the activation of oxygen in the support, which is a key step in the CO oxidation process, determines the shape of the curve. This oxygen
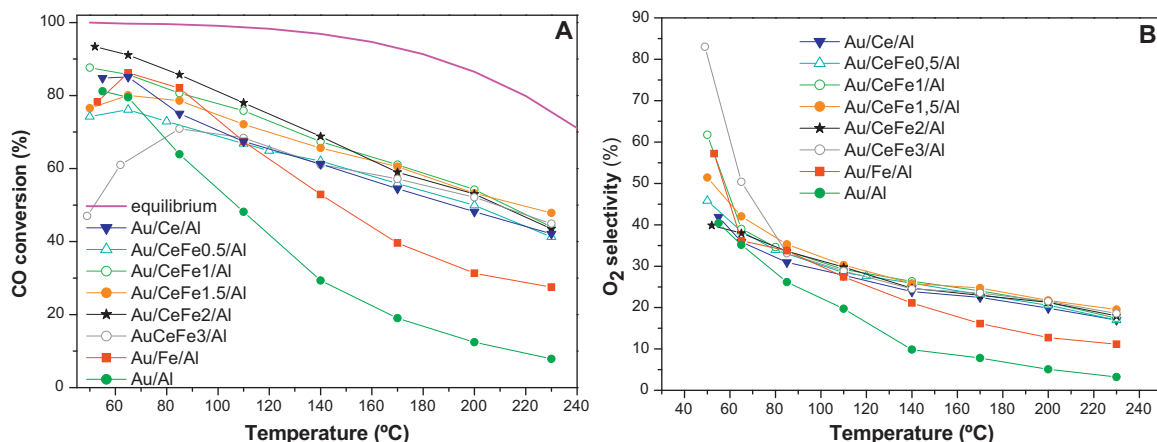
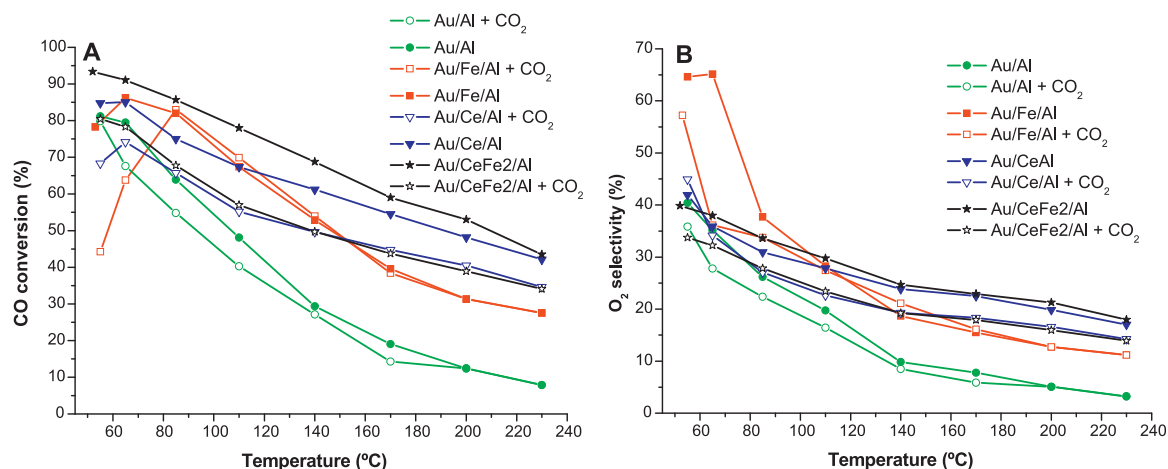**Fig. 1.** Catalytic PROX screening; (A) CO conversion; (B) O_2 selectivity.

Fig. 2. Influence of CO_2 in the PROX stream; (A) CO conversion; (B) O_2 selectivity. Reaction mixture: 1% CO; 1.5% O_2; 50% H_2; 10% CO_2 balanced in N_2.

activation is enhanced in the ceria-based samples due to a higher amount of structural defects in the ceria lattice, especially when iron is incorporated thus modulating both activity and selectivity.

3.2. Influence of CO_2 and H_2O

To study the effect of CO_2 in the series of catalysts, 4 samples were selected: Au/Al (binary system), Au/Ce/Al, Au/Fe/Al (ternary systems) and Au/CeFe2/Al (quaternary system). The effect of CO_2 on activity and selectivity is analyzed in Fig. 2A and B, respectively. The presence of CO_2 in the gas mixture has a negative effect on both oxygen selectivity and CO conversion. The Au/Al catalyst was the less sensitive in CO_2 presence. Regarding the ternary systems, CO_2 affects more dramatically Au/Ce/Al than Au/Fe/Al in the temperature range 90–120 °C. Moreover, the negative effect of CO_2 in Ce and Fe systems seems to be an additive effect since the quaternary Au/CeFe2/Al system is the most affected by the presence of CO_2. As discussed in previous reports [25–27] the detrimental effect of CO_2 may be due to the competitive adsorption of CO (or H_2) and CO_2 on the catalyst surface. The nature of the support is thought to affect the catalyst behavior in the presence of CO_2; acidic supports seem to be more resistant to deactivation than basic ones [28]. Generally, the intrinsic acid–base properties of ceria containing materials depend on the oxidation state of the cerium cations, with Ce^{3+} being a weaker acid than Ce^{4+}. Considering the highly reducing atmosphere of the PrOx reaction, the presence of Ce^{3+} species is expected. Actually XANES data revealed that ceria evolves

from Ce^{4+} to Ce^{3+} during the WGS reaction, which involves also a reducing atmosphere [29]. These reduced cerium species may give rise to the formation of stable carbonates (according to Pearson acidity [30] the interaction between Ce^{3+}, a soft acid and CO_3^{2-}, a soft base would produce a stable covalent bond) and this can be the reason of the strong inhibition of the CO conversion caused by CO_2. As for the iron promoted ceria sample, not only cerium carbonates but also iron ones ($FeCO_3$) should be considered. These species may block anionic sites on the support where oxygen adsorption occurs [31].

The influence of water was studied in the most active catalyst (Fig. 3A and B). The addition of water involved a decrease on activity (Fig. 3A) and selectivity (Fig. 3B). The curves show that the detrimental effect of water is not as strong as the one observed by CO_2. As was proposed for CO_2, water could manifest a competitive adsorption behavior with CO for the active sites. In addition, the possible competition of water with oxygen for the electron-rich sites in the support where oxygen activation takes place should not be disregarded. This effect could also account for the decrease on the catalytic activity when water is included in the reaction mixture. In principle, the presence of water could generate via WGS reaction a beneficial effect in terms of CO abatement [32], although it also implies an additional hydrogen production, which competes with CO for the oxygen in the stream. Irrespectively the competitor molecule (CO_2, H_2O or H_2) CO adsorption sites will be less available and CO oxidation activity necessarily decreases. The simulation of a real reformate stream with the inclusion of both H_2O and CO_2
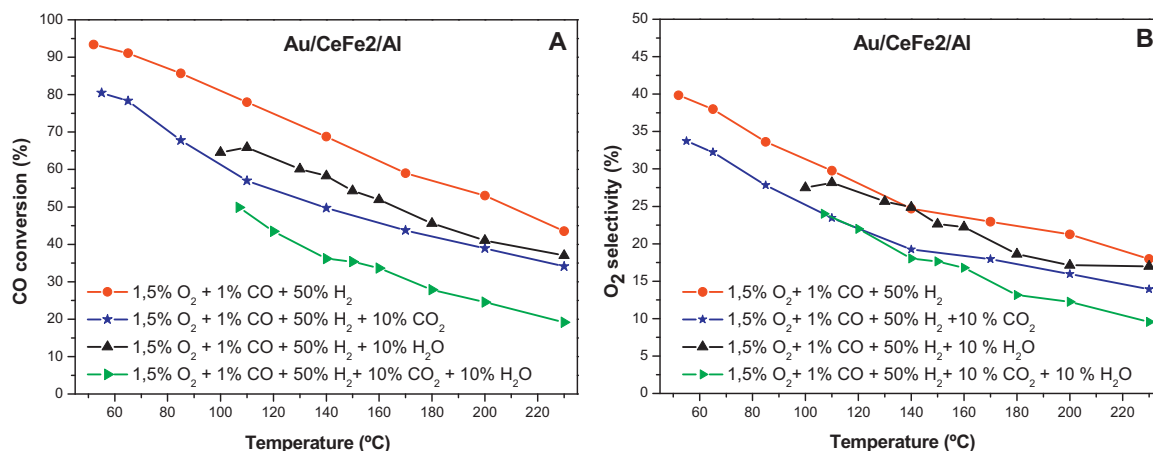

Fig. 3. Influence of water and CO_2 in the PROX behavior of the most active catalyst; (A) CO conversion; (B) O_2 selectivity.
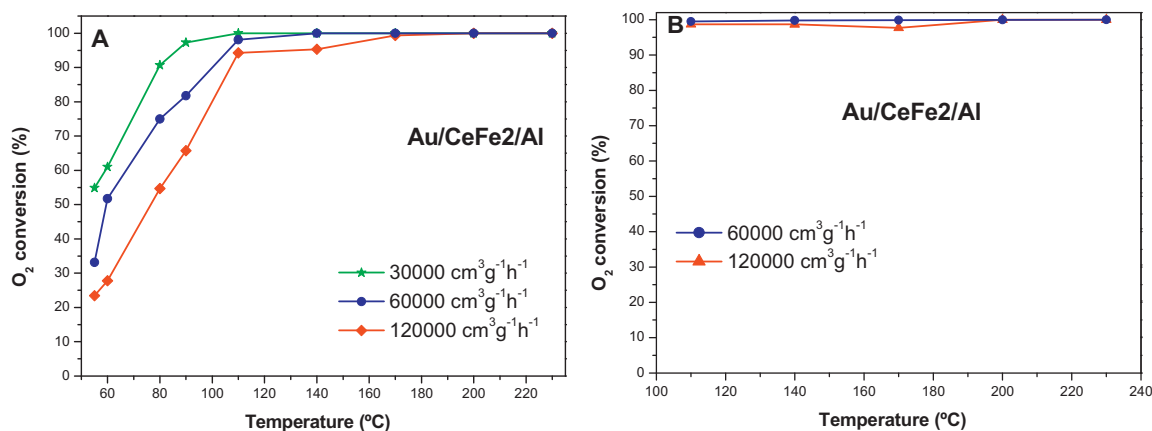
Fig. 4. H_2 oxidation test of the most active catalyst; (A) dry conditions (gas mixture: 1.5% O_2; 50% H_2 balanced in N_2); (B) H_2 oxidation in the presence of water (gas mixture: 1.5% O_2; 10% H_2O, 50% H_2 balanced in N_2).

in the input stream was also evaluated (Fig. 3A and B). The catalytic performance is highly affected by the presence of these two species, leading to a drop of almost 40% in CO conversion at 100 °C. The negative effect of CO_2 and H_2O seems to be cumulative. The decrease in both activity and selectivity of the PrOx catalysts, due to the competitive adsorption of CO, CO_2 and H_2O on the catalyst surface has been broadly reported [33–36]. Again a decrease on the O_2 activation rate due to the competition of oxygen with water and carbon dioxide should be considered. However, it seems that the deactivation is not attributed to any physicochemical modification of the catalysts, since the activity is fully recovered by switching to a H_2O–CO_2 free atmosphere. Therefore the activity inhibition observed in a real reformate stream is not irreversible. From the later it be can deduced that the formation of carbonates species is not the only factor that explains the loss of activity. Lee et al. [37], demonstrated for a CuO_x/CeO_2 model catalyst that the rate of the CO and H_2 oxidation reactions depends on the partial pressure of CO_2 and H_2O resulting in negative reaction orders with respect to these compounds which agrees with our results.

3.3. Carbon monoxide and hydrogen oxidation

Deeper insights of the CO and H_2 oxidation competition could be obtained if both processes are studied separately. Figs. 4 and 5 summarize the data obtained when these two oxidation processes are carried out individually. Because of the large error in the quantification of water and the small change in hydrogen concentration due to the large excess of this compound, oxygen conversion has been selected for the comparative study of H_2 combustion activity. Fig. 4A presents the oxygen conversion during hydrogen combustion at different space velocities. The curves show that hydrogen oxidation starts from the very beginning at low temperatures and total oxygen consumption was achieved in all cases. It was observed that the hydrogen oxidation activity decreases when the space velocity is increased. Full oxygen conversion (or in other words, maximum hydrogen combustion) was reached at 110 °C and 30,000 cm³ g⁻¹ h⁻¹ while total oxidation of hydrogen at 120,000 cm³ g⁻¹ h⁻¹ was achieved at slightly higher temperatures.

The catalytic behavior of the Au/CeFe2/Al in the CO oxidation reaction is presented in Fig. 5. Taking into account the oxygen and the carbon monoxide input (1.5% and 1% respectively) the maximum expected O_2 conversion is 33% when full CO conversion is obtained. The oxygen consumption increases with the contact time. The lower the space velocity, the higher the O_2 conversion is at the same temperature (Fig. 5A). Regarding CO abatement, the same tendency was observed, CO oxidation

increases when the space velocity decreases. Full CO conversion has been reached in all the experiments at about 140 °C (Fig. 5B). Comparing Figs. 4 and 5A, very relevant information can be extracted regarding CO and H_2 competition for the oxygen available in the stream. At 120,000 cm³ g⁻¹ h⁻¹ and at low temperatures, for example 55 °C, 25% of the introduced oxygen was consumed in CO oxidation (maximum possible value of 33%, taking into account, that for lambda parameter of 3 only 1/3 of the oxygen can be consumed for CO oxidation), which corresponds to almost 80% of selectivity towards CO oxidation. At the same time only 21% (maximum possible value of 100%) of oxygen was consumed in hydrogen oxidation. The later reinforces the idea that the CO oxidation is favored at low temperatures but the rate of hydrogen oxidation increases with the temperature.

Another interesting point to comment is that CO oxidation at low temperatures seems to be favored by the presence of H_2. As it can be observed, the CO oxidation activity in the PrOx reaction of this sample at 60 °C is about 90% CO conversion (Fig. 1A) while the CO conversion on the CO oxidation at the same temperature is 60% (Fig. 5B). Generally, the CO oxidation rate decreases in the presence of hydrogen for gold-based systems [38,39]. The negative effect is normally attributed to the competitive adsorption of CO and H_2 on the catalyst surface. However, Rossignol and co-workers observed a boosting effect in CO oxidation activity when H_2 was introduced in the reaction mixture [40]. In their work, they point out that molecular oxygen can be transformed through reaction with hydrogen into active species e.g., hydrogen peroxy-like compounds capable of oxidizing CO. Recently, DFT studies have supported the beneficial effect of H_2 on CO oxidation over gold containing systems [41]. In this study, they propose the formation of OOH species on the support due to the reaction of O_2 with H. The OOH species dissociates easily resulting in the formation of active oxygen for CO oxidation. The later correlates with our results, where H_2 promotes the CO-PrOx activity in the low temperature range. In this context, a good PrOx catalyst has to be paradoxically also active in the H_2 oxidation or at least in the H_2 dissociation. H_2 oxidation in the presence of water is also worth to consider (Fig. 4B). We have tested the activity of the Au/CeFe2/Al sample in the hydrogen oxidation including water in the feed stream. As can be seen in Fig. 4B, full conversion of oxygen was achieved in the whole studied temperature range regardless of the space velocity used. According to these results it can be established that the presence of H_2O does not affect the H_2 oxidation in the studied temperature range. Nevertheless the results obtained for the CO oxidation in the presence of steam (Fig. 5C) revealed that the presence of H_2O decreases the CO oxidation activity. Under dry conditions (Fig. 5B) total CO conversion
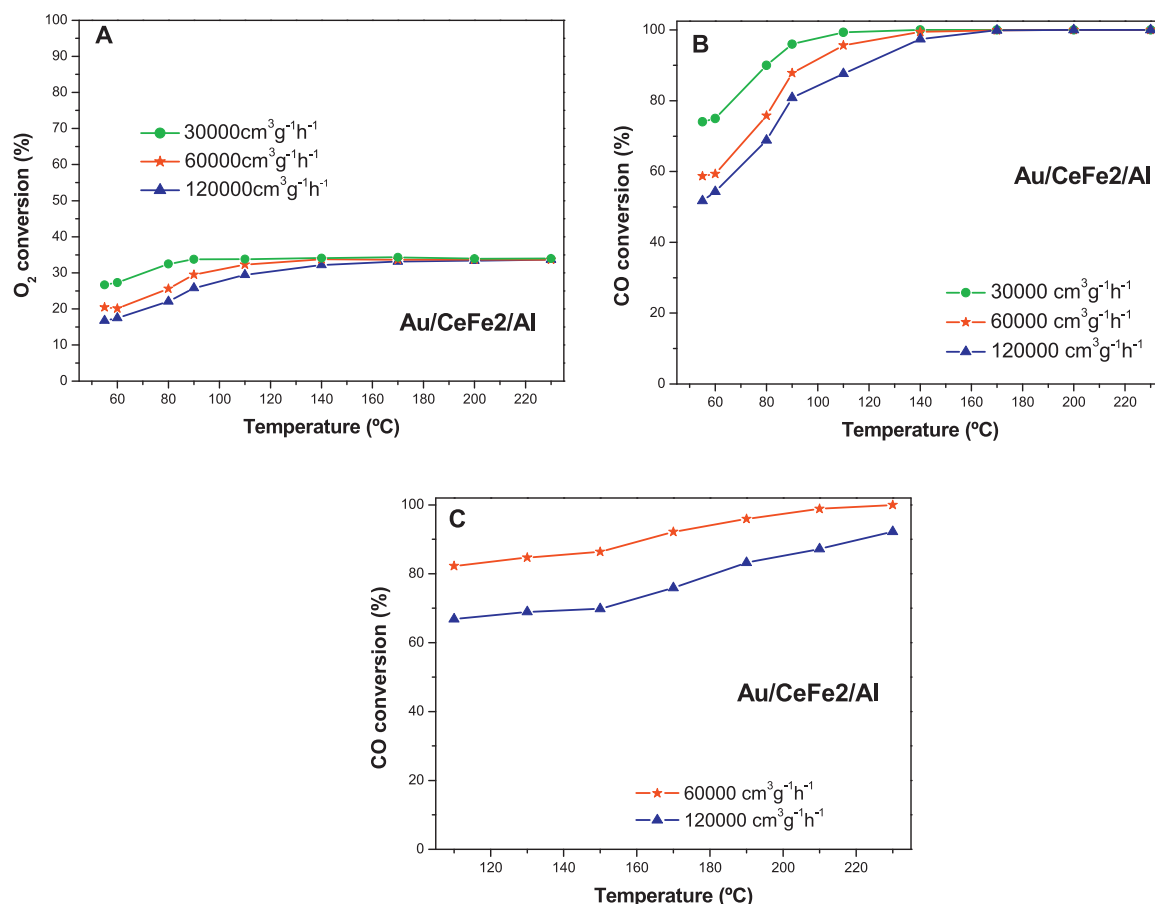
Fig. 5. CO oxidation test of the most active catalyst; (A) O_2 conversion in dry conditions (gas mixture: 1.5% O_2; 1% CO balanced in N_2); (B) CO conversion in dry conditions (gas mixture: 1.5% O_2; 1% CO balanced in N_2); (C) CO conversion under steam (gas mixture: 1.5% O_2; 1% CO 10% H_2O balanced in N_2).

was obtained at 140 °C for all contact times studied, however the inclusion of water in the reactants mixtures remarkably shifts the activity window. Total CO conversion was achieved at 230 °C and 60,000 $cm^3\,h^{-1}\,g^{-1}$ while for higher space velocities this point was not reached. From these results it can be established that water does compete with CO and O_2 or at least, blocks the CO adsorption sites in the catalyst surface decreasing the CO oxidation activity.

3.4. Influence of WGS and RWGS

All these data reveal that the addition of water to the PrOx stream (Fig. 3) alters the CO oxidation activity. In order to elucidate the effect of the possible parallel reactions, the water gas shift and the reverse water gas shift (RWGS) reactions were examined under PrOx conditions (temperature window 110–230 °C and similar space velocity) using the Au/CeFe2/Al sample. As an excellent WGS catalyst, activity in these processes is expected in the 160–350 °C temperature range and indeed some activity for both reactions at temperatures below 150 °C was found. In the case of the WGS the catalyst reached 14% of CO conversion at 230 °C, which is a high value taking into account the space velocity (60,000 $cm^3\,g\,cat^{-1}\,h^{-1}$). As for the RWGS also some activity was detected with 4.1% of CO_2 conversion at 230 °C. According to these data both WGS and RWGS reactions are expected to contribute above 200 °C.

3.5. Pulse experiments

Very interesting information concerning H_2/CO competition was deduced from pulse experiments, which are summarized in Fig. 6. In good agreement with the activity data, CO oxidation is favored at low temperatures. At 30 °C (Fig. 6A) every CO pulse is accompanied with a CO_2 signal accounting for the oxidation of CO. Hydrogen combustion was not observed at 30 °C. Nevertheless H_2 oxidation could not be totally discarded since at this temperature the corresponding peak of water may not appear due to the possible adsorption of water in the catalyst surface. It seems that CO is preferentially adsorbed on the catalysts at this temperature and the inclusion of hydrogen does not displace it, being CO oxidation the reaction that will proceed. However, on increasing the temperature to 90 or 150 °C (Fig. 6B and C, respectively) the competition of both molecules for adsorption on the catalyst increases provoking a noticeable loss of CO oxidation yield. CO is no longer able to remove H_2 molecules from the catalyst surface. In fact, at these temperatures, after three H_2/CO pulses, CO oxidation is almost negligible pointing that H_2 adsorption prevails over CO adsorption influencing the selectivity of the process. These results correlate with the activity data presented in Fig. 1A for this Au/CeFe2/Al sample, where a decreasing tendency on CO conversion was observed. The pulse experiments easily demonstrate that the selectivity towards CO oxidation necessarily diminishes with temperature due to the competitive CO/H_2 adsorption on the catalyst surface. It should be noted that these experiments have been carried out in the absence of oxygen and, therefore, CO and H_2 oxidation took place with oxygen provided by the catalysts (most probably oxygen from the ceria lattice). Further important information regarding the inhibitory effect of CO_2 is extracted from Fig. 6D. Here the sample was treated first with ten O_2 pulses (not shown in the figure) and after that some CO pulses were sent. CO oxidation was observed by the formation of CO_2 (circle 1 in the figure). Afterward, some O_2 pulses were sent
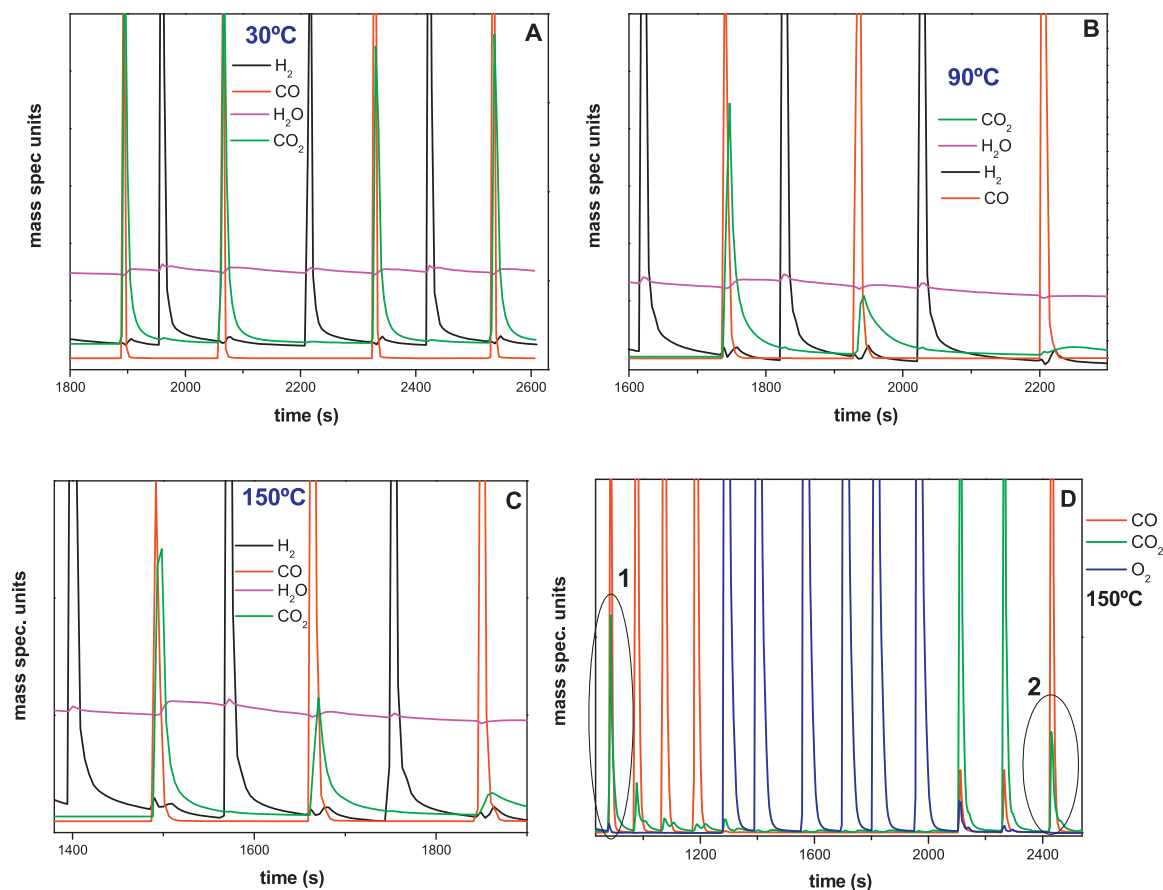
Fig. 6. CO/H_2 pulses experiment; (A) sequence of CO (red lines)/H_2 (black lines) pulses at 30 °C; (B) Sequence of CO/H_2 pulses at 90 °C; (C) sequence of CO/H_2 pulses at 150 °C; (D) effect of CO_2. For all the cases CO and H_2 oxidation are followed by the apparition of CO_2 (olive line) and H_2O (magenta line) signals. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

again to recover the original situation and subsequently two CO_2 pulses were sent in order to saturate the catalyst surface. CO was flowed just after CO_2 and the CO oxidation activity in terms of CO_2 formation notoriously decreased (circle 2). The area of the CO_2 peak produced in this situation was half the one obtained in situation 1 pointing that CO oxidation activity is two times higher when CO_2 is not present. The later confirms the hypothesis that CO_2 blocks the oxygen activation sites limiting the catalytic performance in the PrOx reaction in good agreement with the activity results discussed above.

3.6. Effect of lambda and space velocity

Frequently, from the industrial point of view, selectivity is more important than activity. We have tried to improve the activity/selectivity balance by modulating the λ parameter. The activity and selectivity data obtained for different λ values are presented in Fig. 7A and B, respectively. CO conversion and O_2 selectivity show opposite trends on changing λ. The higher the value of λ, the higher the CO conversion and lower the O_2 selectivity is.

This behavior evidences the high activity of gold for both CO and H_2 oxidation that has been discussed above. For low lambda values, lower CO conversion was obtained but at high selectivity because the majority of the available oxygen reacts preferentially with CO than with H_2 especially at low temperatures, as observed in the independent CO and H_2 oxidation tests. For high lambda values, high activity for both CO and hydrogen oxidation was observed, thus decreasing the selectivity. It is worth to point out that the differences in selectivity when lambda is changed are more

significant at low temperatures (60–90 °C), where the CO oxidation is favored. However, when the temperature is increased, H_2 oxidation becomes important even for low lambdas values. Finally it must be underlined that there are no differences in terms of CO conversion between λ = 3 and λ = 4 confirming that λ = 3 is an optimum value.

The contact time is also a point to consider for improving the conversion/selectivity ratio. Fig. 8A and B show the influence of space velocity on the conversion and selectivity of the selected Au/CeFe2/Al catalyst. The conversion and selectivity follow the same tendency, the higher the WHSV, the lower the conversion and selectivity. In other words, the conversion/selectivity balance can be improved by increasing the contact time between the reactive molecules and the catalyst. It should be noted that better selectivity values can be achieved at low temperatures with 30,000 $cm^3\,g^{-1}\,h^{-1}$ instead of 12,000 $cm^3\,g^{-1}\,h^{-1}$ suggesting that 30,000 $cm^3\,g^{-1}\,h^{-1}$ could be the optimum space velocity. However, the higher CO conversion was obtained for the lowest space velocity. This observation is directly correlated with the tendency presented in the WGS reaction where the lower the space velocity, the higher the CO conversion [22].

3.7. Influence of O_2/CO and the H_2O/CO_2

Finally, in an attempt of arriving at the best conversion/selectivity balance, the influence of the O_2/CO (Fig. 9A) and the H_2O/CO_2 (Fig. 9B) ratios in a simulated reforming stream at the optimum value of 30,000 $cm^3\,g^{-1}\,h^{-1}$ WHSV and the temperature at 110 °C was studied. Fig. 9A suggests that the best
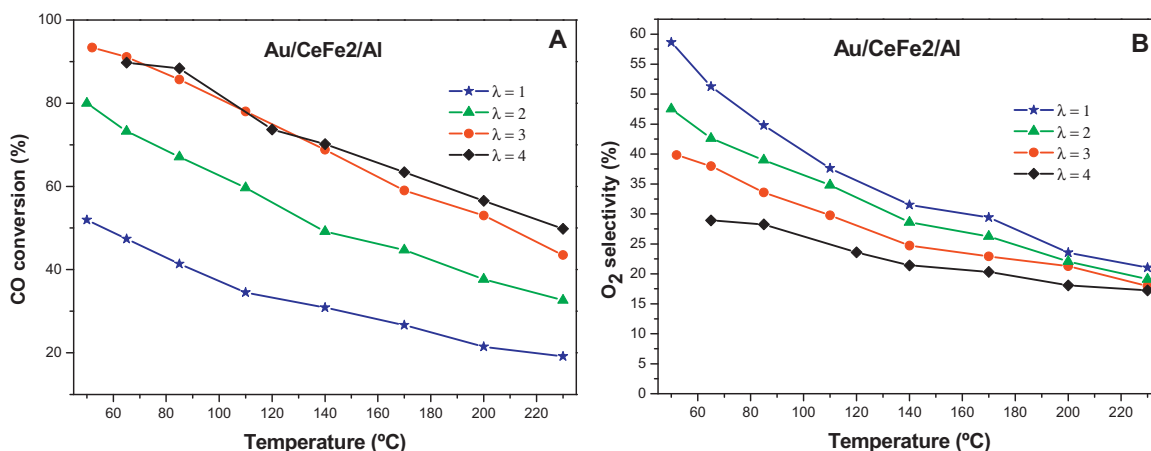
Fig. 7. Effect of λ parameter in (A) activity and (B) selectivity of the most active catalyst. Experiments carried out at 60,000 cm³ g⁻¹ h⁻¹ and in the absence of H_2O and CO_2 in the stream.
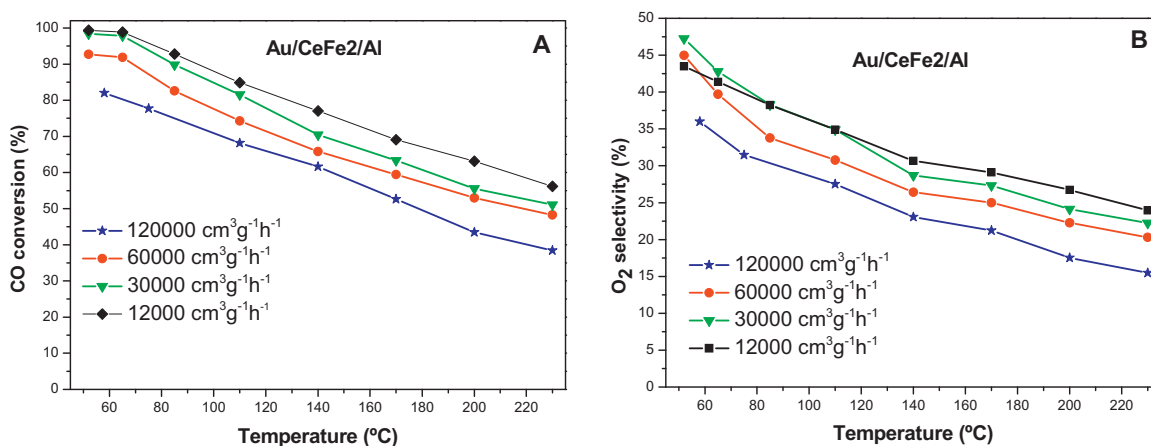

Fig. 8. Effect of WHSV in (A) activity and (B) selectivity of the most active catalyst. Experiments carried out at λ = 3 and in the absence of H_2O and CO_2 in the stream.

conversion/selectivity balance in these realistic conditions is achieved for a λ value of 2.5 whereas the CO conversion is 53% with an oxygen selectivity value of 27%. Concerning H_2O/CO_2, Fig. 9B reveals that the CO conversion and the O_2 selectivity increase with increase of this ratio. Taking into account that both CO_2 and H_2O inhibit the activity, CO_2 being the strongest inhibitor, it seems that water mitigates the CO_2 detrimental effect. Part of CO could be also consumed by the water gas shift reaction, enhancing the global CO oxidation activity.

3.8. Influence of CO concentration

To confirm this hypothesis, PrOx reaction in a realistic reforming stream using different amounts of CO in the inlet was evaluated and the results are presented in Fig. 10. Very relevant information is extracted from the CO conversion trend in Fig. 10A. The increase of the CO concentration, dramatically improves the CO conversion. For low carbon monoxide levels, 0.5 and 1 v/v % (typical CO concentrations in the PrOx reactor inlet), the conversion is low and
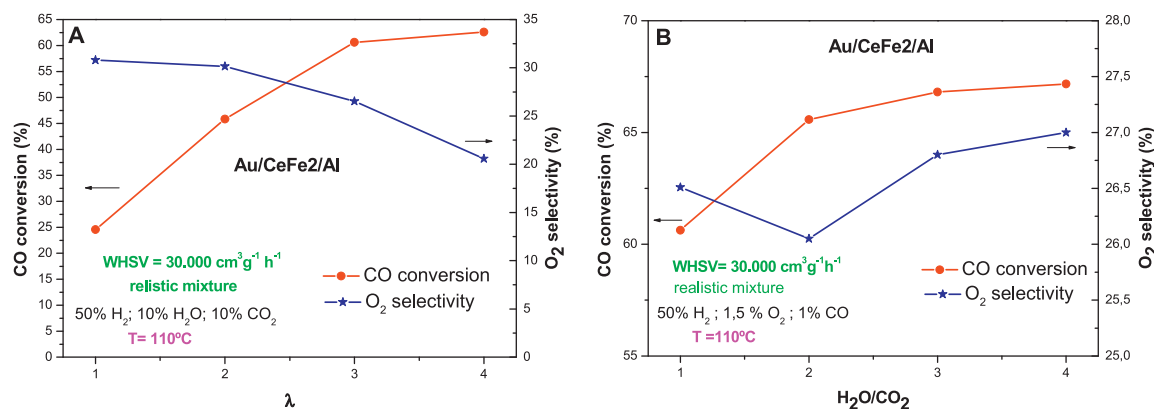

Fig. 9. Influence of the O_2/CO (A) and H_2O/CO_2 B) ratios in a simulated reforming stream at selected WHSV and temperature.
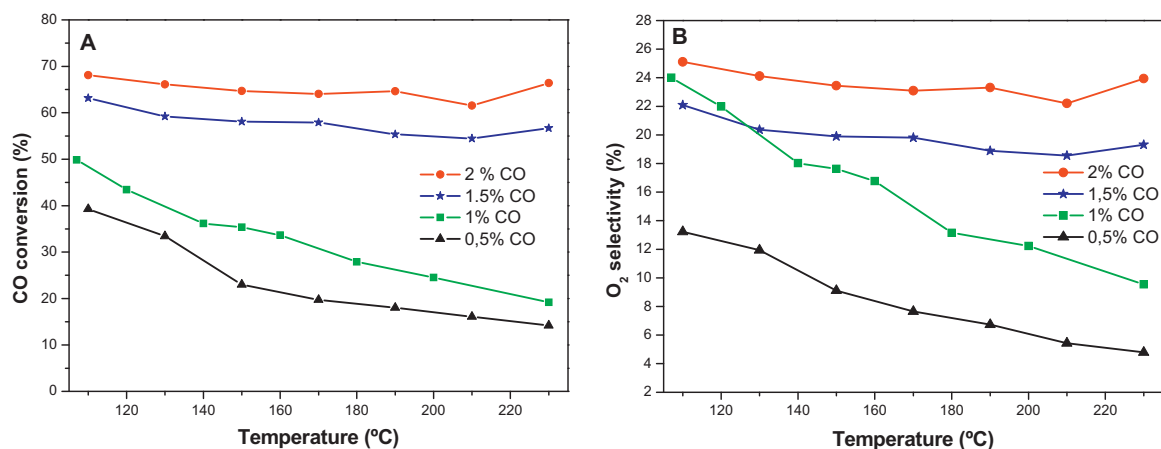
Fig. 10. Influence of CO concentration (at $\lambda = 3$ and $60{,}000 \, cm^3 \, g^{-1} \, h^{-1}$); (A) CO conversion; (B) O_2 selectivity. Experiments carried out in the presence of 10% of CO_2 and 10% of H_2O.

decreases with the temperature. Nevertheless, for higher CO levels (1.5 and 2 v/v %), the conversion is remarkably superior and remains stable with temperature. In other words, when the reaction conditions approach those of the WGS reaction (high CO and H_2O concentrations), CO oxidation is favored confirming that a part of CO abatement takes place via WGS due to the suitability of this Au/CeFe2/Al sample for the shift reaction. Similar beneficial effect was found for the selectivity values (Fig. 10B). The increase of the CO amount in the feed is associated to the increase on the selectivity towards CO_2 indicating that the competition among CO and H_2 oxidation is sensitive to the amount of CO due to the WGS influence and the higher surface coverage of CO at high CO concentration in the feed. This is a very promising result considering the idea of coupling WGS and PrOx since, in the case of a not very successful WGS step, a high concentration of CO will be introduced in the PrOx unit and this catalyst tolerates large amounts of CO.

From all the above, relevant information can be extracted in order to address the main issue of this work; could these efficient WGS catalysts be successfully used in the PrOx reaction? It is not that easy to find a definite answer. It has been demonstrated in this work that a gold catalyst supported on ceria–iron mixed oxide is very active in CO oxidation in the presence of H_2 but its selectivity is limited especially in the high temperature range. In addition, the approach to a real reformate stream limits the CO oxidation activity of this system. It seems that this catalyst does not successfully tolerate the presence of H_2O and CO_2, especially CO_2, but this detrimental effect could be mitigated with increase of the [H_2O/CO_2] ratio, which leads to an increase on the activity and selectivity. Moreover, a relevant point to consider is that this catalyst works more efficiently at high CO concentrations whereas CO evidently competes more favorably than hydrogen for the active sites. Overall, it can be concluded that Au/CeFe2/Al could effectively oxidizes CO in a H_2-rich stream as long as the reaction would occur at the lowest temperature and space velocity possible, the highest H_2O/CO_2 ratio, uppermost CO concentrations and a properly modulated λ value. Under the mentioned reaction conditions the best activity/selectivity balance is obtained for this kind of catalysts.

4. Conclusions

The possible application of a highly effective WGS series of catalysts in the PrOx reaction for H_2 clean up processes has been investigated. All the prepared solids are very efficient for CO oxidation in the presence of hydrogen especially at low temperatures in an ideal PrOx atmosphere (CO_2 and H_2O free). The inclusion of CO_2

and H_2O in the stream involves a loss of activity, with CO_2 being the strongest inhibitor.

The study of CO and H_2 oxidation separately revealed that both molecules do compete for the oxygen in the stream. CO oxidation is favored at low temperatures, however these gold-based catalysts are also able to oxidize H_2 at low temperatures. The ability of the samples to oxidize H_2 limits the selectivity of the process. However, the presence of H_2 increases the CO oxidation activity most probably due to the formation of additional reactive intermediates in the presence of hydrogen.

As a final remark, an excellent WGS catalyst like the Au/CeFe2/Al system could also be a promising catalyst for the PrOx reaction. Nevertheless, it has to be taken into account that the conditions of both processes (temperature window, space velocity, and amount of H_2O, CO, CO_2 and H_2) are different and therefore, a careful modulation of the reaction parameters is required for a successful coupling of both reactions with the same catalyst. Even by modulating the reaction parameters, our systems are not able to satisfy the demanding requirements of fuel cells and further investigations are needed to achieve this goal with the same catalyst via WGS and PrOx. However this study provides some clues towards the future development of such a multirole catalyst. In particular with our catalysts, higher CO oxidation yields are achieved when the reaction conditions get closer to those of the WGS (higher amounts of CO and lower space velocities). Also the increase of the [H_2O]/[CO_2] ratio promotes both activity and selectivity. According to the promoted CO oxidation activity due to the influence of the WGS reaction the presented catalysts should be especially useful in CO-rich PrOx atmospheres.

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